

Sorption of micropollutant estrone to a water treatment ion exchange resin

Peta A. Neale^a, Maibritt Mastrup^b, Thomas Borgmann^b and Andrea I. Schäfer^{a*}

^aSchool of Engineering and Electronics, The University of Edinburgh,
Edinburgh, EH9 3JL, United Kingdom

^bIngeniørhøjskolen Odense Teknikum, Niels Bohrs Alle 1,5230 Odense M, Denmark

Submitted to
Journal of Environmental Monitoring – Special Issue 'Water'
July 2009
Resubmitted August 2009

* Corresponding author: Andrea Schäfer, E-mail: Andrea.Schaefer@ed.ac.uk, Ph: +44(0)131 650 7209; Fax: +44(0)131 650 6781

Abstract

Micropollutants occur in natural waters from a range of sources. Estrogenic compounds are naturally excreted by humans and hence stem predominantly from wastewater effluents. Due to the small size and concentration of such micropollutants their removal is difficult. In this study a technology – magnetic ion exchange (MIEX[®]) - developed to remove natural organic matter from surface water, was investigated. Estrone interacts with polymeric materials such as ion exchange resins or membranes through a number of mechanisms including specific and non-specific interactions. To understand the mechanisms and subsequent implications of this interaction sorption and desorption of estrone was studied as a function of pH, temperature, natural organic matter concentration, sulfate concentration and ionic strength. The results demonstrated that the resin removed around 70% estrone at high pH conditions (>10.4) when estrone was predominantly negatively charged. However, below pH 10.4, when estrone was neutral, approximately 40% of estrone still sorbed due to hydrogen bonding. The optimum temperature for estrone sorption was observed to be from 15 to 35 °C, while the presence of other anions had implications for estrone removal due to competition for anion exchange sites. Desorption of estrone was most effective with 2 M NaCl regeneration brine concentration when estrone was negatively charged (98% desorption). However, when estrone was neutral there was no significant difference between 1 M and 2 M NaCl. The results presented in this study indicate that polar non-ionic micropollutants were removed by magnetic ion exchange due to sorption to the resin polymer. Consequently, this study has implications for improved understanding of micropollutant removal by such resins. Beyond the possibilities of exploiting ion exchange for the removal of micropollutants, the accumulation of micropollutants on polymeric materials in water treatment is a potential risk to be monitored.

Keywords: Magnetic ion exchange (MIEX[®]), natural organic matter, micropollutant, sorption, desorption, water treatment

Introduction

Water treatment processes are increasingly designed to remove dissolved contaminants and micropollutants that reach water supplies from various sources. Natural organic matter (NOM), for example, poses a significant problem in water supplies as disinfection processes transform these natural compounds into hazardous disinfection by-products. In consequence, a strong base anion exchange resin (AER) that can remove such NOM (weak acidic ions predominantly) has been developed. An example of an AER is magnetic ion exchange resin (MIEX[®]) which is a polyacrylate macroporous polymer with strong base quaternary ammonium functional groups for ion exchange¹ and a magnetic iron oxide core to assist with resin agglomeration and recovery.² This resin can be used to remove other contaminants also, such as bromide, sulfate, nitrate, arsenic and chromium,^{3,4} and the process can further be used to control fouling in membrane filtration, where NOM plays an important role. The process can be retrofitted to existing water treatment plants that were not designed to remove NOM and may be environmentally and energetically beneficial over more advanced treatment.

Micropollutants, such as natural and synthetic hormones, pesticides and pharmaceutically active products, are ubiquitous in the aquatic environment, and can be considered a cause of concern for human and environmental health.⁵ Estrone is a naturally excreted steroidal hormone, which can also be formed through the oxidation of estradiol.⁶ Natural hormones such as estrone have the potential to disrupt the endocrine system and consequently have implications for fertility and reproductive health.^{7,8} Studies have shown that low concentrations of estrone (3 ng/L) can cause behavioural changes in some aquatic organisms.⁹ Removal of estrone by conventional sewage treatment plants is variable. A study by Carballa et al.¹⁰ found higher concentrations of estrone in wastewater effluent compared to the influent concentration due to estradiol degradation, while other studies have observed average removals of 53-61%.¹¹⁻¹³ As a result, estrone is regularly detected in surface waters and sewage effluents at low ng/L concentrations.^{14,15}

As conventional treatment cannot completely remove micropollutants such as estrone, other removal technologies have been explored including ozonation, advanced oxidation processes and membrane filtration, particularly nanofiltration/reverse osmosis (NF/RO). Studies have demonstrated that estrone can be removed to below detectable limits using ozonation¹⁶⁻¹⁸ and ClO₂ oxidation¹⁹, while Nghiem et al.²⁰ found estrone retention by NF/RO membranes varied from 13 to >90% due to differences in membrane properties. While very few studies exist on the removal of hormones by ion exchange (IX) resins, Zhang and Zhou²¹ found moderate removal of estrone from solution using a styrene IX resin, with 71 hours required to reach equilibrium. Environmental effects like temperature or water quality such as pH has not been considered.

Micropollutant removal mechanisms of IX resins other than ion exchange of charged molecules are to date not well understood. Humbert et al.⁴ studied the removal of pesticides atrazine and isoproturon using a range of strong AERs. The study showed pesticide removal ranged from 5-37% for all AERs, however MIEX[®] could only remove 5-7% of pesticides.⁴ The low removal was attributed to the non-ionic nature of the pesticides in the experimental conditions. Despite this, specific and non-specific interactions, such as hydrophobically assisted ion exchange and hydrogen bonding, can occur between neutral acidic species such as phenolic groups (at pH 7) and the polymer.^{22,23} The porous nature of the resin can assist with the removal of neutrally charged contaminants.²⁴ It is also likely that non-ionic micropollutants can interact with the resin polymer through hydrogen bonding²⁵, increasing potential non-ionic micropollutant uptake. While micropollutant removal is generally a desired phenomenon in water treatment, it can also occur as a side effect with accumulation of micropollutants on the resin and concentration in the brine.

The resin is regenerated using a NaCl brine which exchanges any anions sorbed to the quaternary ammonium functional group for chloride ions.²⁶ Caustic compounds such as NaOH can be added to the NaCl brine to enhance desorption. It is to date not understood if regeneration only reverses micropollutants removed by ion exchange or also other sorption processes.

The purpose of the study is to investigate the removal as well as partitioning mechanisms of estrone and to assess the influence of water chemistry parameters such as pH and ionic strength. As estrone is predominately negatively charged at pH > 10.4, studying the influence of pH on estrone removal can improve understanding of both ion exchange and specific and non-specific interaction mechanisms. Temperature effects as well as estrone removal in the presence of competing ions, such as NOM and sulfate, will be studied to understand the influence of competition. Finally, the release of estrone from the resin during regeneration will be investigated in order to understand any associated treatment liabilities and risks concerning accidental contamination of water as well as the potential presence of micropollutants in brines following their accumulation on the resin.

Experimental

Chemicals

All chemicals used are of analytical grade. Radiolabelled [2,4,6,7-³H]estrone was purchased from Sigma Aldrich (Saint Louis, US). Estrone is a bipolar hormone, with an acid dissociation constant (pK_a) of 10.4.²⁷ The background electrolyte was 1 mM NaHCO₃. The pH was adjusted using 1 M HCl and 1 M NaOH. Natural organic matter (NOM), from Brisbane Water National Park in Australia, was concentrated using microfiltration and RO, and was extensively characterised by Schäfer.²⁸

Magnetic ion exchange resin (MIEX®)

The resin was supplied by Orica Watercare (Melbourne, Australia). The concentration of resin used in the experiment was 10 mL/L. Industrial applications typically use doses ranging from 2 to 20 mL/L²⁹, however, previous studies have indicated that a dose of 8-10 mL/L is optimal for NOM and inorganic anion removal.^{4,26}

Sorption experiments

The sorption experiments were conducted in 100 mL Erlenmeyer flasks containing 50 mL of MilliQ water with 1 mM NaHCO₃ background electrolyte. The initial estrone concentrations were 1, 5, 10, 50, 100 and 500 ng/L, which is in the range of typical surface and wastewaters. Erlenmeyer flasks were placed in a temperature controlled Bioline incubator shaker (Alexandria, Australia). Before each experiment 1 mL from each flask was removed for analysis, and 0.5 mL (0.113 g) of resin slurry was added to each flask using 5 mL single use syringes, giving a total concentration of 10 mL/L. Flasks were shaken for 2 hours at 200 rpm, and a sample of 1 mL was collected. Adsorption kinetics reached equilibrium within 25 minutes. In the pH sorption experiments the pH was adjusted to 3, 5, 8, 9, 10, 11 and 12 using 1 M HCl and NaOH and the temperature was kept constant at 25 °C. In the temperature experiments the temperature was adjusted to 15, 25, 35, 45 and 55 °C at pH 8. The NOM, ionic strength and sulfate experiments were studied at pH 8 and 11 and a constant temperature of 25 °C. The NOM concentrations studied were 0, 10, 30 and 100 mg/L (0, 0.63, 1.89, 6.3 mgC/L), while in the ionic strength sorption experiments NaCl concentrations of 0, 20, 50, 100 and 200 mM were studied. For the sulfate experiments the SO₄²⁻ concentrations were 0, 5 and 20 mM.

The desorption experiments were also conducted in 100 mL Erlenmeyer flasks following the 100 ng/L estrone sorption experiments at pH 7, 8, 9, 10 and 11. The resin was allowed to settle and the supernatant was decanted and 50 mL of MilliQ water was added. The effect of ionic strength using NaCl concentrations of 0, 1 and 2 M was studied. The pH was adjusted to 7, 8, 9, 10 and 11. 1 mL

of initial solution was removed for analysis. The flasks were shaken in the incubator shaker at 200 rpm for 1 hour and samples of 1 mL were collected at 2, 5, 10, 15, 30 and 60 minutes.

Analysis

Scintillation counting was used to detect estrone at very low concentrations. Samples from sorption and desorption experiments (1 mL) were added to 9 mL of Ultima Gold LLT scintillation cocktail (Perkin Elmer, Boston, US) and shaken until clear. The samples were taken after the resin had settled and analysed using a Packard Instruments Tri-Carb® liquid scintillation counter (2100 TR, Boston, US) where they were left to count for 5 minutes each. The activity in counts per minute (cpm) was converted to estrone concentration in ng/L. The percentage of estrone removal by sorption is calculated using Equation 1, while the mass of estrone removed per mass of resin is calculated using Equation 2. The sorption isotherms are calculated as the mass of estrone removed per mass of resin as a function of the estrone equilibrium concentration. This represents the freely dissolved hormone concentration in solution at equilibrium. The percentage of estrone desorbed with the addition of NaCl brine can also be calculated using Equation 1.

$$\text{Sorption } (\%) = 1 - \frac{C_E}{C_I} \cdot 100\% \quad (1)$$

$$Q_E = \frac{(C_I - C_E) \cdot V_W}{M_{IX}} \quad (2)$$

Where: C_E is the concentration of estrone at equilibrium (ng/L)
C_I is the initial concentration of estrone prior to resin addition (ng/L)
Q_E is the mass of estrone removed per mass of resin (ng/g)
V_W is the solution volume (L)
M_{IX} is the mass of resin added (g)

A field emission scanning electron microscope (Hitachi s-900 FESEM) at 20 kV was used to image the resin.

Results and discussion

Characteristics of MIEX®

Within the literature, the resin beads are suggested to have an average diameter of 150 to 180 µm, which is approximately 2 to 5 times smaller than other commonly used IX resins.³⁰ As a result, it has a greater surface area to volume ratio compared to larger IX resins thus increasing micropollutant removal.³¹ However, the average diameter of the resin in Figure 1 appears to be considerably less than what is suggested in the literature, with particles as small as 5 to 10 µm observed. Therefore, it is likely that the resin is susceptible to mechanical break-up. The charge of the resin is unlikely to be influenced by solution pH, as the quaternary ammonium functional groups give the resin a positive charge in both acidic and alkaline solutions.

[Figure 1]

Sorption

To understand the sorption mechanisms of charged and uncharged estrone the influence of pH is studied. pH can influence the speciation and charge of estrone as it has a pK_a of 10.4. This has implications for the transport and behaviour of estrone within natural and engineered systems as charge can influence hormone removal.²⁷ The removal of uncharged estrone from pH 3 to 10 is similar (Figure 2a), with approximately 40% removal. At pH 11 and 12 when estrone is negatively

charged, estrone removal increases substantially to 60-70%. Figure 2b shows the mass of estrone sorbed per mass of resin as a function of pH, and this also indicates a significantly increased isotherm slope at pH 11 and 12

[Figure 2]

Due to the strong base quaternary ammonium functional groups, the resin has a strong pH tolerance³², and hence observed changes in estrone removal can be attributed to the dissociation of estrone. Estrone is 99.5% protonated at pH 8 and is 82-97% dissociated at pH 11 and 12. As the dominant removal mechanism for the resin is ion exchange, estrone removal is greatest when estrone is predominantly negatively charged at pH > 10.4 (Figure 3). However, at pH values lower than the pK_a, moderate estrone removal by also observed (40%) which is surprising. The removal of non-ionic estrone can be explained with physical interactions such as van der Waals forces and hydrogen bonding with the polyacrylate polymer.²² The mechanism of interaction is likely to be absorption, compared to adsorption, due to the resin material. The polyacrylate coating is similar to the coating of some fibres used for solid-phase microextraction (SPME), and studies have indicated that micropollutants are removed by such SPME fibres through absorption.³³ Further, the linearity of the sorption isotherms in Figure 2b suggests that absorption is indeed the dominant mechanism.³⁴

[Figure 3]

The significant removal of non-ionic estrone suggests that hydrogen bonding is the dominant physical sorption mechanism. Estrone contains a phenolic hydroxyl group which acts as a hydrogen donor and acceptor, hence it is bipolar, and a ketone group which is a strong hydrogen acceptor.³⁵ The polyacrylate resin also contains polar functional groups such as ketone and ammonium moieties, and therefore hydrogen bonding is indeed possible. Previous studies have observed strong estrone sorption to membrane polymers and it is suggested that this is due to hydrogen bonding, as well as non-specific interactions.^{27,36} Schäfer et al.²⁷ found estrone sorption to the membrane polymers significantly decreased as the pH exceeded the pK_a and hydrogen bonding capacity decreased. In the case of the resin, the dissociation of estrone adds the potential of ion exchange, which is indeed observed.

Temperature is of interest as it may have implications for micropollutant removal kinetics. As estrone is non-ionic at pH 8, removal by the resin is due to physical sorption. The removal of estrone as a function of temperature is shown in Figure 4a. The removal of estrone is similar from 15 to 35°C, with average removals ranging from 36-40%. As the temperature increases to 45°C the average estrone removal decreases to 31%, and to 23% at 55°C. The sorption isotherms (Figure 4b) indicate a similar mass of estrone removed per mass of resin from 15 to 35°C.

[Figure 4]

The effect of temperature on NOM removal by magnetic ion exchange resin has been studied previously. Humbert et al.⁴ studied NOM removal from 6 to 36°C and found no difference in removal between 6 and 26°C, however removal increased as the temperature increased at 36°C due to accelerated kinetics. In contrast, Semmens et al.³⁷ compared NOM removal by the resin in summer (24°C) and winter (6°C) conditions and found a 12% reduction in NOM removal in colder conditions due to slower NOM uptake. Chen³⁸ found that NOM removal was similar at 25°C and 35°C with a polyacrylic IX resin. The variations in the literature are due to different experimental conditions, such as equilibrium time and resin doses. However, at pH 8 estrone is not interacting with the resin through ion exchange, as NOM does, therefore it is difficult to compare these results or identify a coherent mechanism. Similar to this study, a decrease in micropollutant uptake by polyacrylate SPME fibres have previously been observed at high temperatures.³⁹ As sorption to

polyacrylate is diffusion controlled, the temperature accelerates removal kinetics.⁴⁰ However, as the temperature increases to 45 and 55°C the polyacrylate-water partition coefficient decreases³⁹, and this may lead to a reduction in estrone removal at high temperatures.

The sorption of estrone is also studied in the presence of varying NOM, ionic strength and sulfate concentrations. NOM and sulfate are selected as they may compete with estrone for ion exchange binding sites, while ionic strength has implications for charge shielding and hence can affect the ion exchange process. Experiments are conducted at pH 8 and 11 to study the influence of estrone dissociation on removal. In Figure 5a the isotherm slope decreases as NOM concentration increases at pH 8, indicating a reduction in estrone removal with increasing NOM concentration. However, there appears to be no significant difference in sorption at pH 11 (Figure 5b). This change in sorption is related to estrone charge. As estrone is neutrally charged at pH 8 it can only be removed through physical interactions, while the anionic NOM can be removed through ion exchange, which is a stronger interaction. Therefore, as more NOM is removed less estrone can be sorbed by the resin. It is likely this is due to the significantly higher NOM concentration (10-100 mg/L compared to 1-500 ng/L) which can block estrone sorption sites. However, at pH 11 when estrone is negatively charged it can out-compete NOM for binding sites, therefore there is no significant difference in estrone sorption with increasing NOM concentration. Ion exchange to the macroporous IX resin is diffusion controlled⁴¹, therefore estrone out-competes NOM due to the significantly lower molecular weight of estrone (270.4 g/mol versus <1000 g/mol) which results in a greater diffusion constant.

[Figure 5]

The influence of ionic strength (NaCl) is studied as it may shield electrostatic interactions between estrone and the resin functional groups.⁴² Figure 6a shows for pH 8 a slight decrease in estrone sorption in the presence of 20 mM NaCl, however there is no difference in isotherm slope as the ionic strength increases from 20 mM to 200 mM NaCl. For pH 11 a significant reduction in isotherm slope with increasing ionic strength is observed, indicating decreasing estrone sorption (Figure 6b). At high ionic strength the charge of estrone and resin functional groups are shielded reducing the ion exchange capability, resulting in decreasing sorption as a function of ionic strength at pH 11. Below the pK_a of estrone the high ionic strength did not influence the sorption, as ion exchange is not the removal mechanism.

[Figure 6]

Sulfate is a multivalent anion (SO₄²⁻), and previous studies indicate that the presence of sulfate can reduce the removal of organic matter as it can compete for anion exchange sites.^{22,43} Consequently, the influence of estrone removal in the presence of sulfate is studied to determine if this influences estrone removal. Figure 7a shows a reduction in isotherm slope in the presence of sulfate for pH 8, while in Figure 7b little difference in estrone sorption at pH 11 is observed when ion exchange occurs. Similar to NOM, the concentration of sulfate is considerably higher (**4-1850×10⁻⁹** mM of estrone versus 5-20 mM of sulfate) reducing estrone sorption sites at pH 8.

[Figure 7]

Desorption

IX resins are regenerated through reverse ion exchange, where contaminants are substituted for, in this case, chloride ions (Figure 8).⁴⁴ It is unknown if micropollutants, such as estrone, can be removed from the resin by regeneration, and for this reason the influence of ionic strength on estrone desorption as a function of pH is measured using MilliQ water (0 M), 1 M and 2 M NaCl (Figure 9). Desorption is lowest in MilliQ water with 33-42% desorption, followed by 1 M NaCl

with 59-67% estrone desorption and 58-98% at 2 mM. In both MilliQ water and 1 M NaCl the resin appears to demonstrate some degree of regeneration meaning that the contaminants are likely to desorb if the water quality varies, and that ion exchange is not the mechanism as there is no chlorine in MilliQ water. This indicates that pure water may be contaminated by micropollutants sorbed to the resin. At 2 M NaCl from pH 7 to 10 desorption is similar to 1 M NaCl with 58-62% desorption. At pH 11, when estrone is 82% negatively charged, there is 98% desorption of estrone, indicating that an ionic strength of 2 M is sufficient to regenerate the negatively charged estrone. No difference in desorption as a function of pH is observed for MilliQ water or 1 M NaCl, suggesting that regeneration is a NaCl concentration dependent process.

[Figure 8]
[Figure 9]

Conclusions

The improved removal of steroidal hormones such as estrone from water and wastewater is of great importance. The application of MIEX[®] to remove estrone is influenced by the solution chemistry, temperature and the presence of competing anions. When estrone is negatively charged, the resin can remove as much as 70% of estrone, and up to 98% can be desorbed using NaCl. However, at neutral pH values, more common in wastewater treatment applications, the removal is significantly less (40%), with desorption up to 67%. Results imply that the application of the resin combined with another water treatment mechanism, such as membrane filtration or advanced oxidation, may be a good and energy efficient option to ensure significant removal of charged micropollutants from water. An important implication of this study is that polymeric resins are likely to concentrate micropollutants resulting in an elevated concentration in the resin material and the brines from regeneration processes. The disposal and treatment of such brines require solid future investigation, as does the risk of release of micropollutants if ionic strength or pH of vary accidentally.

Acknowledgements

Orica Watercare (Melbourne, Australia) are thanked for provision of MIEX[®] sample. Professor Menachem Elimelech is thanked for revisions of the manuscript during his time in Edinburgh as Royal Academy of Engineering Distinguished Visiting Fellow.

References

1. C. J. Johnson and P. C. Singer, *Water Res.*, 2004, **38**, 3738-3750.
2. T. H. Boyer and P. C. Singer, *Water Res.*, 2005, **39**, 1265-1276.
3. A. K. Jha, A. Bose and J. P. Downey, *Sep. Sci. Technol.*, 2006, **41**, 3297-3312.
4. H. Humbert, H. Gallard, H. Suty and J.-P. Croué, *Water Res.*, 2005, **39**, 1699-1708.
5. R. P. Schwarzenbach, B. I. Escher, K. Fenner, T. B. Hofstetter, C. A. Johnson, U. von Gunten and B. Wehrli, *Science*, 2006, **313**, 1072-1077.
6. G. G. Ying, R. S. Kookana and Y.-J. Ru, *Environ. Int.*, 2002, **28**, 545-551.
7. S. Jobling, M. Nolan, C. R. Tyler, G. Brightly and J. P. Sumpter, *Environ. Sci. Technol.*, 1998, **32**, 2498-2506.
8. S. Jobling, S. Coey, J. G. Whitmore, D. E. Kime, K. J. W. Van Look, B. G. McAllister, N. Beresford, A. C. Henshaw, G. C. Brightly, C. R. Tyler and J. P. Sumpter, *Biol. Reprod.*, 2002, **67**, 515-524.
9. C. A. Murphy, N. E. Stacey and L. D. Corkum, *J. Chem. Ecol.*, 2001, **27**, 1573-1561.
10. M. Carballa, F. Omil, J. M. Lema, M. Llompard, C. García-Jares, I. Rodríguez, M. Gómez and T. Ternes, *Water Res.*, 2004, **38**, 2918-2926.
11. A. C. Johnson, A. Belfroid and A. Di Corcia, *Sci. Total Environ.*, 2000, **256**, 163-173.

12. M. R. Servos, D. T. Bennie, B. K. Burnison, A. Jurkovic, R. McInnis, T. Neheli, A. Schnell, P. Seto, S. A. Smyth and T. A. Ternes, *Sci. Total Environ.*, 2005, **336**, 155-170.
13. G. D'Ascenzo, A. Di Corcia, A. Gentili, R. Mancini, R. Mastropasqua, M. Nazzari and R. Samperi, *Sci. Total Environ.*, 2003, **302**, 199-209.
14. D. W. Kolpin, E. T. Furlong, M. T. Meyer, E. M. Thurman, S. D. Zaugg, L. B. Barber and H. T. Buxton, *Environ. Sci. Technol.*, 2002, **36**, 1202-1211.
15. C. Baronti, R. Curini, G. D'Ascenzo, A. Di Corcia, A. Gentili and R. Samperi, *Environ. Sci. Technol.*, 2000, **34**, 5059-5066.
16. T. A. Ternes, J. Stüber, N. Herrmann, D. McDowell, A. Ried, M. Kampmann and B. Teiser, *Water Res.*, 2003, **37**, 1976-1982.
17. M. M. Huber, T. A. Ternes and U. von Gunten, *Environ. Sci. Technol.*, 2004, **38**, 5177-5186.
18. H. Zhang, H. Yamada and H. Tsuno, *Environ. Sci. Technol.*, 2008, **42**, 3375-3380.
19. M. M. Huber, S. Korhonen, T. Ternes and U. von Gunten, *Water Res.*, 2005, **39**, 3607-3617.
20. L. D. Nghiem, A. Manis, K. Soldenhoff and A. I. Schäfer, *J. Membr. Sci.*, 2004, **242**, 37-45.
21. Y. Zhang and J. L. Zhou, *Water Res.*, 2005, **39**, 3991-4003.
22. Y. Tan and J. E. Kilduff, *Water Res.*, 2007, **41**, 421j1-4221.
23. P. Li and A. K. SenGupta, *React. Funct. Polym.*, 2004, **60**, 27-39.
24. K. Shorrock and B. Drage, *Water Environ. J.*, 2006, **20**, 65-70.
25. B. Bolto, D. Dixon, R. Eldridge, S. King and K. Linge, *Water Res.*, 2002, **36**, 5057-5065.
26. M. Kitis, B. I. Harman, N. O. Yigit, M. Beyhan, H. Nguyen and B. Adams, *React. Funct. Polym.*, 2007, **67**, 1495-1504.
27. A. I. Schäfer, L. D. Nghiem and T. D. Waite, *Environ. Sci. Technol.*, 2003, **37**, 182-188.
28. A. I. Schäfer, *Natural Organics Removal Using Membranes: Principles, Performance, and Cost*, CRC Press, Boca Raton, 2001.
29. J. Y. Morran, M. Drikas, D. Cook and D. B. Bursill, *Water Sci. Technol.: Water Supply*, 2004, **4**, 129-137.
30. P. C. Singer and K. Bilyk, *Water Res.*, 2002, **36**, 4009-4022.
31. A. Nel, T. Xia, L. Mädler and N. Li, *Science*, 2006, **311**, 622-627.
32. T. H. Boyer and P. C. Singer, *Environ. Sci. Technol.*, 2008, **42**, 608-613.
33. W. H. J. Vaes, C. Hamwijk, E. Urrestarazu Ramos, H. J. M. Verhaar and J. L. M. Hermens, *Anal. Chem.*, 1996, **68**, 4458-4462.
34. R. P. Schwarzenbach, P. W. Gschwend and D. M. Imboden, *Environmental Organic Chemistry*, 2nd edn., John Wiley & Sons, Inc., Hoboken, 2003.
35. K.-U. Goss and R. P. Schwarzenbach, *J. Chem. Educ.*, 2003, **80**, 450-455.
36. L. D. Nghiem, A. I. Schäfer and M. Elimelech, *Environ. Sci. Technol.*, 2004, **38**, 1888-1896.
37. M. J. Semmens, M. Burckhardt, D. Schuler, P. Davich, M. Slunjski, M. Bourke and H. Nguyen, American Water Works Association Conference, Denver, 2000.
38. P. H. Chen, *Environ. Int.*, 1999, **25**, 655-662.
39. I. Citová, R. Sladkovský and P. Solich, *Anal. Chim. Acta*, 2006, **573-574**, 231-241.
40. H. Lord and J. Pawliszyn, *J. Chromatogr. A*, 2000, **902**, 17-63.
41. P. Li and A. K. SenGupta, *Environ. Sci. Technol.*, 2000, **34**, 5193-5200.
42. L. D. Nghiem and A. I. Schäfer, *Environ. Eng. Sci.*, 2002, **19**, 441-451.
43. T. H. Boyer and P. C. Singer, *Water Res.*, 2006, **40**, 2865-2876.
44. B. Bolto, D. Dixon and R. Eldridge, *React. Funct. Polym.*, 2004, **60**, 171-182.
45. H. Hubicka and D. Kolodynska, *Hydrometallurgy*, 2001, **62**, 107-113.

List of Figures

- Figure 1:** Field emission scanning electron microscope (FESEM) image of the magnetic ion exchange resin.
- Figure 2:** a) Removal of estrone and b) sorption isotherms for estrone as a function of pH (background electrolyte 1 mM NaHCO₃).
- Figure 3:** Primary mechanisms of estrone removal by anion exchange resin as a) physical sorption and b) ion exchange (adapted from Li and SenGupta²³ and Hubicka and Kolodynska.⁴⁵).
- Figure 4:** a) Removal of estrone and b) sorption isotherms for estrone as a function of temperature (background electrolyte 1 mM NaHCO₃, pH 8).
- Figure 5:** Sorption isotherms for estrone as a function of natural organic matter (NOM) concentration at a) pH 8 and b) pH 11 (background electrolyte 1 mM NaHCO₃).
- Figure 6:** Sorption isotherms for estrone as a function of ionic strength (NaCl) at a) pH 8 and b) pH 11 (background electrolyte 1 mM NaHCO₃).
- Figure 7:** Sorption isotherms for estrone as a function of sulfate concentration at a) pH 8 and b) pH 11 (background electrolyte 1 mM NaHCO₃).
- Figure 8:** Resin regeneration mechanism using NaCl.
- Figure 9:** Desorption of estrone in MilliQ water, 1 M NaCl and 2 M NaCl as a function of pH (background electrolyte 1 mM NaHCO₃).

Figure 1

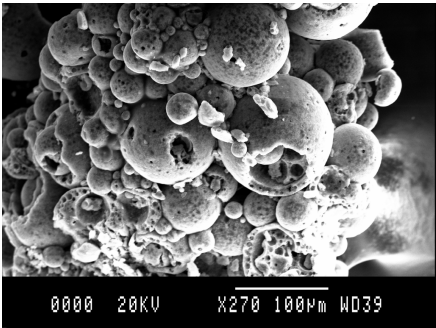


Figure 2

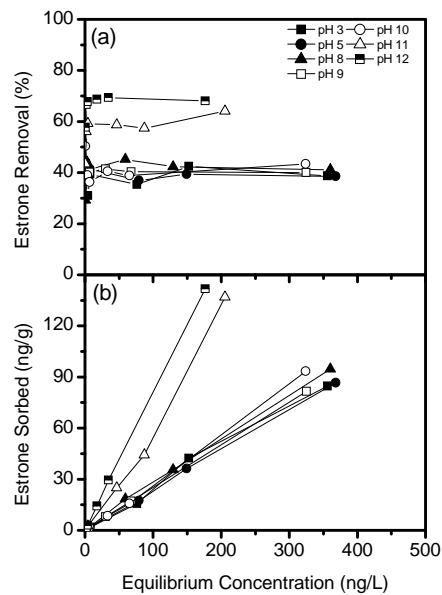


Figure 3

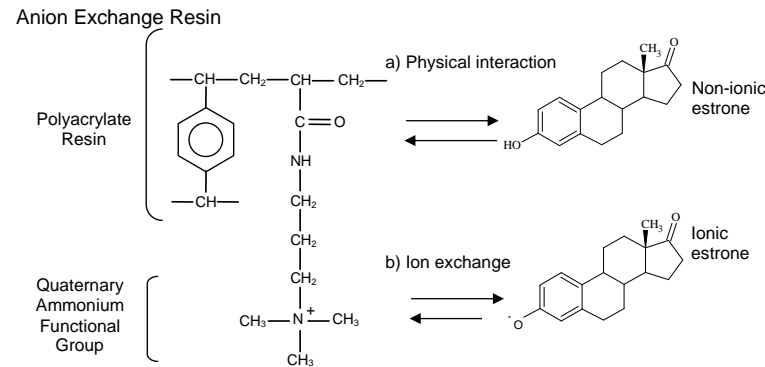


Figure 4

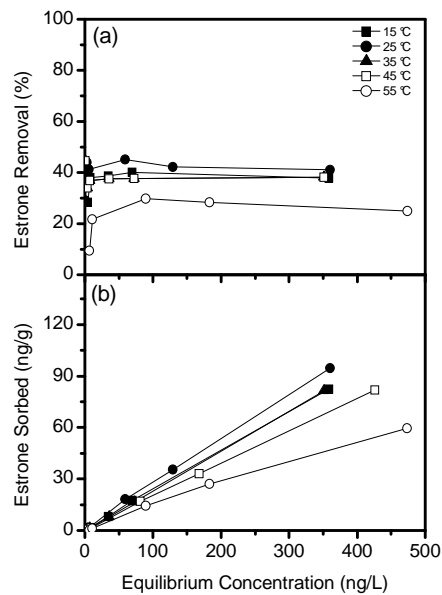


Figure 5

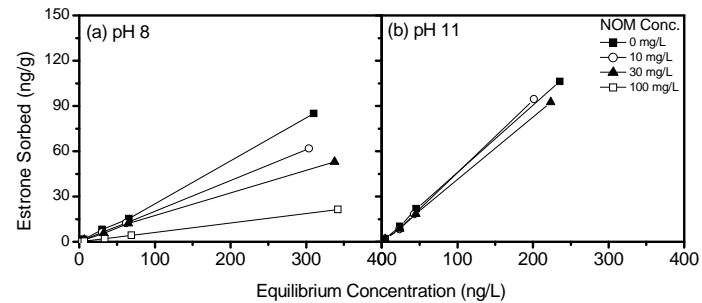


Figure 6

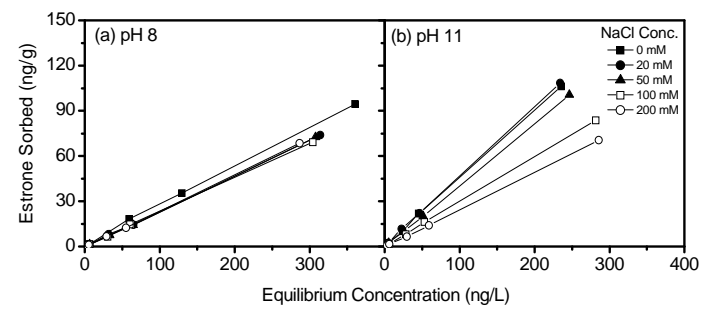


Figure 7

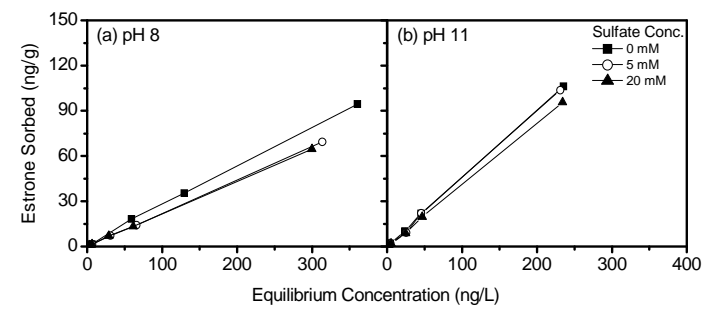


Figure 8

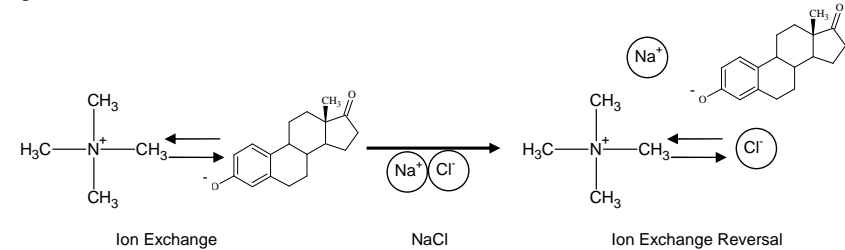


Figure 9

